Chapter 6

Thermodynamics and Bending Energetics of Microemulsions

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Additional information is available at the end of the chapter

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Abstract

A comprehensive, yet simple, theoretical model for droplet microemulsions is presented. The model combines thermodynamics of self-assembly with bending elasticity theory and relates microemulsion properties, such as average droplet size, polydispersity, interfacial tension and solubilisation capacity with the three bending elasticity constants, spontaneous curvature (H_0), bending rigidity (k_c) and saddle-splay constant ($\bar{k}_c$). In addition, the self-association entropy constant (k_s) explicitly determines various microemulsion properties. The average droplet size is shown to increase with increasing effective bending constant, defined as $k_{eff} = 2k_c + \bar{k}_c + k_s$, as well as with decreasing magnitudes of H_0. The polydispersity decreases with increasing values of k_{eff}, but does not at all depend on H_0. The model predicts ultra-low interfacial tensions, the values of which decrease considerably with increasing droplet radius, in agreement with experiments. The solubilisation capacity increases as the number of droplets is increased with increasing surfactant concentration. In addition, an enhanced solubilisation effect is obtained as the size of the droplets increases with increasing surfactant concentration, as a result of self-association entropy effects. It is demonstrated that self-association entropy effects favour smaller droplet size as well as larger droplet polydispersity.

Keywords: surfactant, self-assembly, microemulsion, interfacial tension, solubilisation, spontaneous curvature, bending rigidity, saddle-splay constant

1. Introduction

Surfactants are amphiphilic molecules consisting of a hydrophilic head group and a hydrophobic tail. Surfactants self-assemble above a certain surfactant concentration in an aqueous solvent to form micelles or bilayers. The driving force for the self-assembly process is the tendency to minimize the interfacial contact area between water and surfactant hydrophobic

tails. As a result, the tails make up an interior core of the micelles that is absent of water whereas the hydrophilic head groups are located at the interface adjacent to the aqueous solvent. Hydrophobic components that are usually insoluble in water, such as oil or fat, may be dissolved into a surfactant-water system. The oil molecules become incorporated into the hydrophobic core of the micelles to form swollen micelles. However, there is a limit how much oil that may be dissolved by micelles and above a certain amount of oil two separate liquid phases coexist, i.e. thermodynamically stable oil droplets (discrete phase) dissolved in water (continuous phase) coexisting with excess oil (cf. **Figure 1**). Such an oil-in-water (o/w) microemulsion phase coexisting with an excess oil phase in a two-phase system is denoted as Winsor I microemulsion. Some surfactants, on the other hand, may form reversed water-in-oil (w/o) droplets that dissolve water (discrete phase) in oil (continuous phase) in the presence of excess water (Winsor II microemulsion). Moreover, a microemulsion phase may also coexist with both excess oil and excess water in a three-phase system (Winsor III microemulsion) [1]. A Winsor III microemulsion does not usually consist of finite-sized droplets. Rather some kind of macroscopic structure is formed, either more or less planar alternating layers of oil and water separated by surfactant monolayers, or some kind of ordered or disordered bicontinuous phase with a system of separated tunnels of water and oil [2].

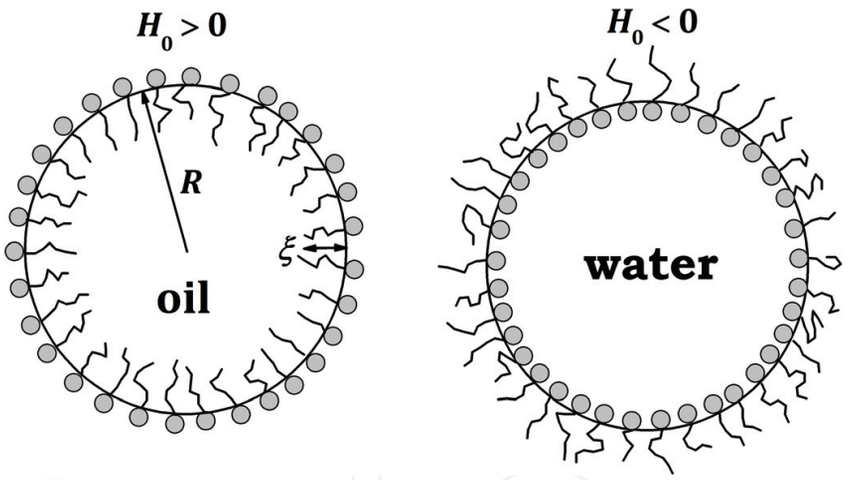

Figure 1. Schematic figures showing a spherical oil-in-water (o/w) microemulsion droplet (left) and a water-in-oil (w/o) microemulsion droplet (right). The radius of the droplet is denoted R and the thickness of the surfactant monolayer at the interface is denoted ξ. Oil-in-water droplets are formed by surfactants with a positive spontaneous curvature ($H_0 > 0$) whereas w/o droplets are formed by surfactants with $H_0 < 0$.

The microscopic structure of microemulsions (whether Winsor I, II or III), is mainly determined by the chemical structure of the surfactant. Surfactants with large hydrophilic head groups and small hydrophobic (or lipophilic if one prefers) parts tend to curve so as to form ordinary micelles or o/w microemulsion droplets whereas surfactants with a small hydrophilic part and large hydrophobic part (like phospholipids) tend to form w/o microemulsion droplets (cf. **Figure 1**). The molecular properties determining the curvature of a surfactant monolayer may be summed up in the quantity hydrophilic-lipophilic balance, or shorter the HLB value [3]. As a result, one expects o/w microemulsion droplets to increase in size as the monolayer becomes less curved

with decreasing HLB values. For sufficiently low HLB values, a transition from Winsor I to Winsor III is expected, and further decreasing HLB would result in the formation of Winsor II microemulsion. In addition to the volume of the hydrophilic and hydrophobic parts, respectively, the presence of electric charge on the surfactant head group also contributes to increase the HLB value and promotes a positive (oil-in-water) curvature of the droplets.

It is possible to tune the HLB value of ionic surfactants by means of adding salt to an aqueous phase and HLB decreases with increasing electrolyte concentration. Similarly, the HLB value of non-ionic ethylene oxide-based surfactants is found to be considerably temperature-sensitive and, as a result, it is possible to observe the sequence of transitions oil-in-water → bicontinuous → water-in-oil microemulsion by means of increasing the temperature [4]. The amount of oil dissolved in the microemulsion increases during this sequence of transitions and, at a certain temperature denoted the phase inversion temperature (PIT), the microemulsion phase contains equal amounts of oil and water. It is also possible to tune the curvature of a surfactant monolayer by means of adding a cosurfactant that is mixed into the layer [5].

In contrast to conventional (macro)emulsions, microemulsions are thermodynamically stable systems. This means that the size of the droplets may fall within a wide range, depending on the surfactant HLB value, from small micelle-like droplets of about 1 nm to about 100 nm, above the size of which the droplets usually transform into a macroscopic bicontinuous structure. In contrast, kinetically stabilized emulsion droplets are usually larger falling in the range 10 nm to 100 μm.

In this chapter, we present a comprehensive, yet simple, theory that rationalizes the structural behaviour of spherical microemulsion droplets. The theory is based on conventional solution thermodynamics combined with bending elasticity theory and it predicts several experimentally available quantities, such as droplet size and polydispersity, interfacial tension and solubilisation capacity. We only consider the case of rather rigid microemulsion droplets that are spherically shaped. More flexible droplets, consisting of interfacial monolayers with bending rigidities approaching zero (see further below), may assume a more spheroidal or ellipsoidal shape [6] or undergo undulatory fluctuations of the droplet interfaces [7].

2. Thermodynamics of self-assembly

Microemulsions are thermodynamically stable equilibrium structures. Hence, the theoretical treatment of microemulsion droplets necessarily needs to take into account thermodynamics of self-assembling surfactant molecules to form an interfacial monolayer that encapsulates the discrete phase (cf. **Figure 1**). The latter process may be considered in terms of a set of multiple equilibrium reactions

$$N \text{ Surfactant} \rightleftharpoons M_N \tag{1}$$

where N is the free surfactant molecules dissolved in the continuous phase (Bancroft's rule states that free surfactants are always present in the continuous phase) that form a microemulsion

droplet M_N. The change in entropy for the process of self-assembling free surfactant molecules to the interface of a single droplet that encloses a certain amount of oil (o/w microemulsions) or water (w/o microemulsions) in accordance with Eq. (1) may thus be written as

$$\Delta S_{agg} = -k(\ln\phi_N - N\ln\phi_{free}) \tag{2}$$

where k is the Boltzmann's constant. For the case of o/w microemulsions, the free surfactant molecules are present in the aqueous continuous phase with a volume fraction ϕ_{free}, whereas oil molecules are brought from the adjacent macroscopic excess oil phase to form droplets encapsulated by surfactant monolayers with volume fraction ϕ_N. The expression in Eq. (2) is also valid for the reverse case of w/o microemulsions in which the surfactant is dissolved in the continuous oil phase and water is brought from an excess aqueous phase. ΔS_{agg} is always a negative quantity and, as a result, the process of self-assembly must be unfavourable in the absence of other contributions favouring the self-assembly process. Equation (2) can be understood as the difference between the entropy of mixing self-assembled surfactant monolayers and solvent, and the entropy of mixing the corresponding amount of free surfactant molecules with solvent.

In order to allow for the spontaneous self-assembly of surfactant molecules, additional contributions to the overall free energy change must be added. These contributions are related to the formation of the surfactant monolayer and can be collected into a single quantity denoted by $\Delta\mu$. The most important contribution to $\Delta\mu$ comes from the hydrophobic effect, i.e. the largely entropic favourable process of reducing interfacial contact between surfactant hydrophobic tails and water molecules as free surfactants are self-assembled in the microemulsion-droplet interfaces. From a molecular point of view, the hydrophobic effect is believed to be the result of organization of water molecules adjacent to the hydrophobic moieties of the surfactant molecules. We may now write the total change in Gibbs free energy of the self-assembly process as

$$\Delta G = N\Delta\mu - T\Delta S_{agg} \tag{3}$$

Introducing the following free energy parameter [8].

$$\mathrm{E}_N \equiv N\Delta\mu - NkT\ln\phi_{free} \tag{4}$$

and combining Eqs. (2)–(4) gives the following set of equilibrium conditions

$$\Delta G_N = \mathrm{E}_N + kT\ln\phi_N = 0 \tag{5}$$

one for each surfactant aggregation number N of the interfacial monolayers. By setting $\Delta G_N = 0$, we account for a situation where surfactant molecules are reversibly exchanged between droplet interface and as free molecules in the continuous phase. Equation (5) may now be rewritten as

$$\phi_N = e^{-\mathrm{E}_N/kT} \tag{6}$$

Summing up the different volume fractions in Eq. (6) gives the total volume fraction ϕ_s of surfactant self-assembled in the droplets, i.e.

$$\phi_s = \sum_{N=2}^{\infty} \phi_N \tag{7}$$

which may be evaluated from the following integral approximation

$$\phi_s = \int_0^{\infty} e^{-\mathrm{E}(N)/kT}\, dN \tag{8}$$

We have been able to approximately set the lower limit in the integral to zero since the largely curved droplets with low aggregation numbers are too energetically unfavourable to contribute to the integral (see further below). Equation (8) gives the full size distribution of surfactants self-assembled in microemulsion-droplet interfaces; in so far an mathematical expression for the function E(N) is available. In the following section, we will demonstrate that such an expression may be obtained by means of considering the properties of bending a surfactant monolayer.

3. Bending elasticity

The free energy of an arbitrarily shaped surfactant monolayer may be calculated taking into account bending elasticity properties. The curvature at a single point on a surfactant monolayer (most conveniently defined at the hydrocarbon/water interface [cf. **Figure 1**]) may be defined by considering two perpendicular curves on the interface with radii of curvature, R_1 and R_2, respectively. Hence, each point at the aggregate interface may be distinguished by two principal curvatures defined as $c_1 = 1/R_1$ and $c_2 = 1/R_2$. By means of changing variables from c_1 and c_2 to the mean curvature $H = ½(c_1 + c_2)$ and Gaussian curvature $K = c_1 \cdot c_2$, respectively, the following fruitful expression for the free energy per unit area may be introduced [9]

$$\gamma(H,K) = \gamma_0 + 2k_c(H - H_0)^2 + \bar{k}_c K \tag{9}$$

The Helfrich expression in Eq. (9) is a second-order expansion with respect to H and K, respectively, and introduces three important parameters, spontaneous curvature (H_0), bending rigidity (k_c) and saddle-splay constant ($\bar{k}_c$). γ_0 is the free energy per unit area at $H = H_0$ and $K = 0$. The total free energy of a surfactant monolayer may be obtained by means of integrating Eq. (9) over the entire interfacial area A of the monolayer giving

$$\mathrm{E} = \int \gamma(H,K)dA = \gamma_0 A + 2k_c \int (H - H_0)^2 dA + \bar{k}_c \int K dA \tag{10}$$

For a spherically curved monolayer, an expression for E is obtained by simply introducing the proper values $H = 1/R$ and $K = 1/R^2$ in Eq. (9) and multiplying γ with the interfacial area $4\pi R^2$. As a result, the following expression for E as a function of droplet radius R is obtained for a surfactant monolayer at the interface of a spherical microemulsion droplet

$$\mathrm{E}(R) = 4\pi(2k_c + \overline{k}_c - 4k_c H_0 R + \gamma_p R^2) \tag{11}$$

where γ_p is the interfacial tension of a strictly planar interface, i.e. $\gamma_p = \gamma(H = K = 0)$. The free energy in Eq. (11) may be considered as a sum of the contribution of forming a planar surfactant monolayer out of free surfactant ($=4\pi R^2\gamma_p$) and the contribution of bending the monolayer into spherical shape.

The three bending elasticity constants H_0, k_c and $\overline{k}_c$ influence various properties of self-assembled surfactant monolayers and are expected to assume values that reflect the chemical properties of the constituent surfactant or surfactant mixture as well as environmental properties such as temperature and electrolyte concentration. They may be interpreted as thermodynamic parameters that may be determined from experiments [10–13] as well as calculated from a suitable molecular model [14–16] by means of minimizing the free energy per molecule of a surfactant interfacial layer at given values of H and K.

3.1. Spontaneous curvature

The spontaneous curvature H_0 represents the sign and magnitude of the preferential curvature of a single surfactant monolayer. Since smaller microemulsion droplets must be more curved than larger ones, H_0 is expected to have a large impact on the droplet size. We have defined the mean and spontaneous curvature of o/w microemulsion droplets as positive, whereas w/o droplets have a negative spontaneous curvature (cf. **Figure 1**). H_0 depends on the chemical structure of a surfactant molecule in so far it is expected to increase with an increasing HLB value [14, 16]. This means that H_0 rapidly decreases as the tail length is increased for a surfactant with given head group. Likewise, ionic surfactants usually have larger spontaneous curvature than non-ionic surfactants with a head group of similar size, and adding electrolyte is expected to reduce H_0 of an ionic surfactant monolayer. As a result, in the presence of both water and oil, surfactants with high HLB values and positive H_0 tend to form o/w microemulsion droplets whereas surfactants with low HLB values and negative H_0 tend to form w/o microemulsions.

3.2. Bending rigidity

The bending rigidity k_c is a measure of the ability of a surfactant monolayer to resist deviations from a uniform mean curvature $H = H_0$. k_c must always be a positive quantity in order to realize a minimum of γ as a function of mean curvature in the Helfrich expression in Eq. (9). Large bending rigidities are expected to favour surfactant monolayers with small deviations from a homogenous curvature, i.e. rigid and monodisperse droplets with a uniform shape. This means that microemulsion droplets are expected to be strictly spherical for sufficiently large values of k_c. Likewise, a bicontinuous microemulsion is expected to form an ordered cubic phase as the bending rigidity is high whereas a more disordered sponge phase forms at low k_c values [17].

From a molecular point of view, it has been demonstrated that k_c assumes a maximum value for some optimal value of the HLB of a surfactant [16]. The flexibility of the surfactant tails appears to have a crucial impact on k_c which is found to be significantly larger for surfactants with a flexible rather than rigid tail [14]. As a matter of fact, it has been demonstrated that k_c must always be equal to zero, thus preventing self-assembly of non-ionic surfactants made up of hydrophobic and hydrophilic parts that both are rigid [16]. For surfactants with a flexible tail, the bending rigidity is expected to increase with increasing tail length [10, 14]. Moreover, k_c has been found to become substantially reduced in surfactant mixtures [18–20] and the magnitude of the reduction has been demonstrated to increase with increasing asymmetry between two surfactants with respect to head group charge number, volume of surfactant tail, etc [15].

3.3. Saddle-splay constant

The saddle-splay constant $\bar{k}_c$ is related to the Gaussian curvature K. As implied by its name, high positive values of $\bar{k}_c$ influence the curvature of an interface so as to favour a saddle-like structure, with negative Gaussian curvature, that is curved in opposite directions perpendicular to one another. Examples of surfactant assemblies with saddle-like structure are torus-like micelles and bicontinuous microemulsions. Hence, the latter is expected to be favoured by large (positive) values of $\bar{k}_c$ whereas a planar lamellar Winsor III microemulsion is favoured by low and negative values of $\bar{k}_c$ [17].

Moreover, according to the Gauss-Bonnet theorem, the last integral in Eq. (10) equals

$$\int K dA = 4\pi(1 - g) \tag{12}$$

where g represents the number of handles or holes present in a surfactant monolayer. A microemulsion droplet consists of one geometrically closed monolayer and, as a result, $g = 0$. As a consequence, the last term in Eq. (10) equals $4\pi\bar{k}_c$, the quantity of which does not depend on the size of the microemulsion droplet. Since $\bar{k}_c$ contributes with a size-independent term to E, the value of $\bar{k}_c$ indirectly determines the size of the droplets. Positive values of $\bar{k}_c$ indicate that the total free energy in the system increases as one single droplet is split up to form two or many smaller droplets. Likewise, negative values of $\bar{k}_c$ imply a decreasing total free energy as droplets are split up to increase their number while maintaining the surfactant concentration fixed. In either case, increasing values of $\bar{k}_c$ favour larger microemulsion droplets.

From a molecular point of view, $\bar{k}_c$ is expected to be negative for a pure symmetric surfactant that tends to curve equivalently in all lateral directions [14]. However, introducing some kind of asymmetry of the surfactant may result in positive values of $\bar{k}_c$. For instance, the non-uniform distribution of charges in monolayers formed by ionic gemini surfactants may result in a positive saddle-splay constant [13, 21]. Likewise, mixtures of two or more asymmetric surfactants, in particular mixtures of oppositely charged surfactants, may result in positive values of $\bar{k}_c$ [22].

4. Microemulsion droplets

The size distribution of surfactant monolayers in Eq. (8) may be rewritten so as to give

$$\phi_s = \int_0^\infty \frac{dN}{dR} e^{-\mathrm{E}(R)/kT} dR = \int_0^\infty \phi_s(R) dR \tag{13}$$

where $\phi_s(R)$ is the volume fraction distribution of surfactant monolayers and

$$\frac{dN}{dR} = \frac{8\pi R\xi}{v} \tag{14}$$

may be evaluated from the geometrical relation $Nv = 4\pi R^2 \xi$ for a surfactant monolayer with thickness ξ and surfactant molecular volume v. However, the self-assembled monolayer is excluded from the interior volume occupied by the discrete phase of oil molecules (in the case of o/w droplets). As a result, it is more appropriate to consider the size distribution based on the volume fraction of entire droplets ϕ_d, including both the surfactant monolayers at the droplet interfaces and solubilised oil molecules in the interior core of the droplets.

The geometrical relations $\phi_d(R) \propto 4\pi R^2 dR$ and $\phi_s(R) \propto 8\pi R\xi dR$ imply that the volume fraction distribution of droplets equals

$$\phi_d(R) = \frac{R}{2\xi} \phi_s(R) \tag{15}$$

Now we may substitute Eq. (11) into Eq. (13) and combine with Eqs. (14) and (15) to arrive at the full size distribution of spherical microemulsion droplets

$$\phi_d(R) = \frac{4\pi R^2}{v} e^{-4\pi(2k_c + \overline{k}_c - 4k_c H_0 R + \gamma_p R^2)/kT} \tag{16}$$

from which the total volume fraction of droplets (including both surfactant and the discrete phase) may be evaluated so as to give

$$\phi_d = \frac{4\pi}{v} e^{-4\pi(2k_c + \overline{k}_c)/kT} \int_0^\infty R^2 e^{-4\pi(\gamma_p R^2 - 4k_c H_0 R)/kT} dR \tag{17}$$

The size distribution according to Eq. (16) is plotted in **Figure 2** for some different values of volume fraction of droplets. In accordance with Eq. (16), the formation of finite-sized microemulsion droplets may be considered as the result of bending elasticity properties as well as self-association entropy effects. The latter contribution always favours small droplets. Since the driving force towards smaller droplets due to the entropy of self-assembly increases in magnitude with decreasing droplet volume fraction, the average size of the droplets depends on ϕ_d and the droplets increase in size with increasing surfactant (or droplet) concentration [cf. further below].

Equation (17) may be solved so as to give

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$$\phi_d = \frac{k_{eff}(kT)^2}{128\pi v(k_c H_0)^3} e^{4\pi k_s/kT}\left(\sqrt{\pi\alpha}(2\alpha+1)(1+erf\sqrt{\alpha})+2\alpha e^{-\alpha}\right) \tag{18}$$

where we have introduced the dimensionless parameter [6, 23]

$$\alpha = \frac{16\pi(k_c H_0)^2}{\gamma_p kT} = \frac{4\pi}{kT}(2k_c + \bar{k}_c + k_s) \tag{19}$$

as well as the quantity

$$k_s = \frac{kT}{4\pi}\ln\left(\frac{128\pi v(k_c H_0)^3\phi_d}{k_{eff}(kT)^2\left(\sqrt{\pi\alpha}(2\alpha+1)(1+erf\sqrt{\alpha})+2\alpha e^{-\alpha}\right)}\right) \tag{20}$$

Except for values of α close to zero, the following two approximations of Eqs. (18) and (20), respectively, are accurate

$$\phi_d = \frac{\pi k_{eff}^{5/2}(kT)^{1/2}}{4v(k_c H_0)^3} e^{4\pi k_s/kT} \tag{21}$$

$$k_s = \frac{kT}{4\pi}\ln\left(\frac{4v(k_c H_0)^3\phi_d}{\pi k_{eff}^{5/2}(kT)^{1/2}}\right) \tag{22}$$

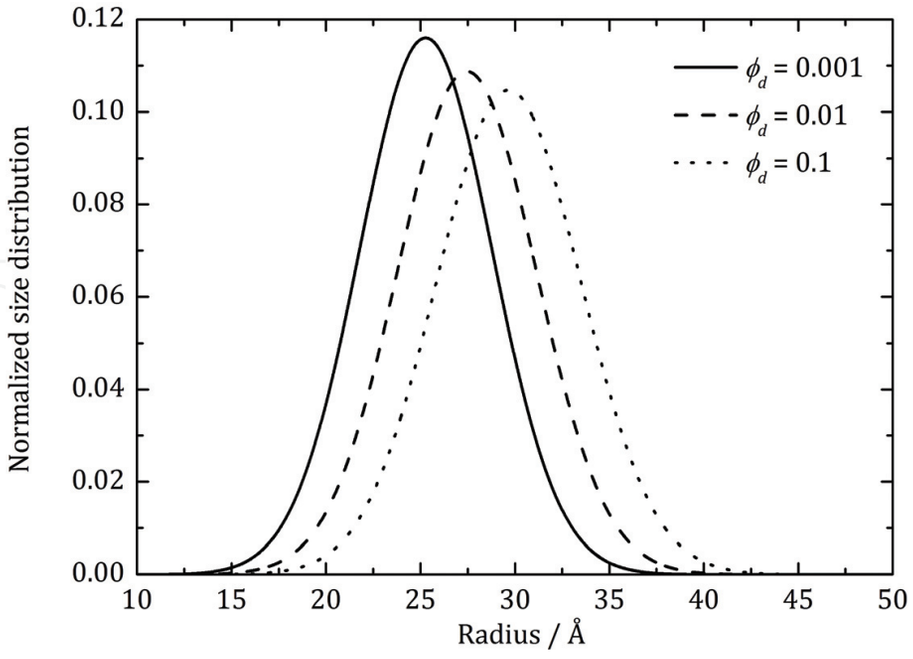

Figure 2. The normalized size distributions of microemulsion droplets at some different values of the droplet volume fraction ϕ_d. The bending elasticity constants were set to $k_c = 1.0kT$, $\bar{k}_c = 0.725kT$ and $\xi H_0 = 0.645$, where $\xi = 17$ Å, as obtained for a gemini surfactant forming elongated micelles in water [13]. The average droplet radii are seen to be always smaller than those expected from the expression $\langle R\rangle = (2k_c + \bar{k}_c)/2k_c H_0 = 36$ Å.

The entropy parameter k_s may be added to the sum of twice the bending rigidity and the saddle-splay constant to make up the effective bending constant $k_{eff} = 2k_c + \overline{k}_c + k_s$. Hence, k_s has a similar impact on microemulsion droplet properties, such as average size and polydispersity (see further below), as k_c and $\overline{k}_c$, although it is not (primarily) related to bending elasticity properties. From a physical point of view, it is a measure of the entropy of self-assembly and, since this process is unfavourable from an entropic point of view, k_s is always found to be a negative property (cf. **Figure 3**). Moreover, the entropy of self-assembly increases in magnitude as the concentration of surfactant decreases. As a result, k_s becomes a strong function of volume fraction of surfactant and its magnitude increases (that is k_s becomes more negative) as a solution of microemulsion droplets is diluted.

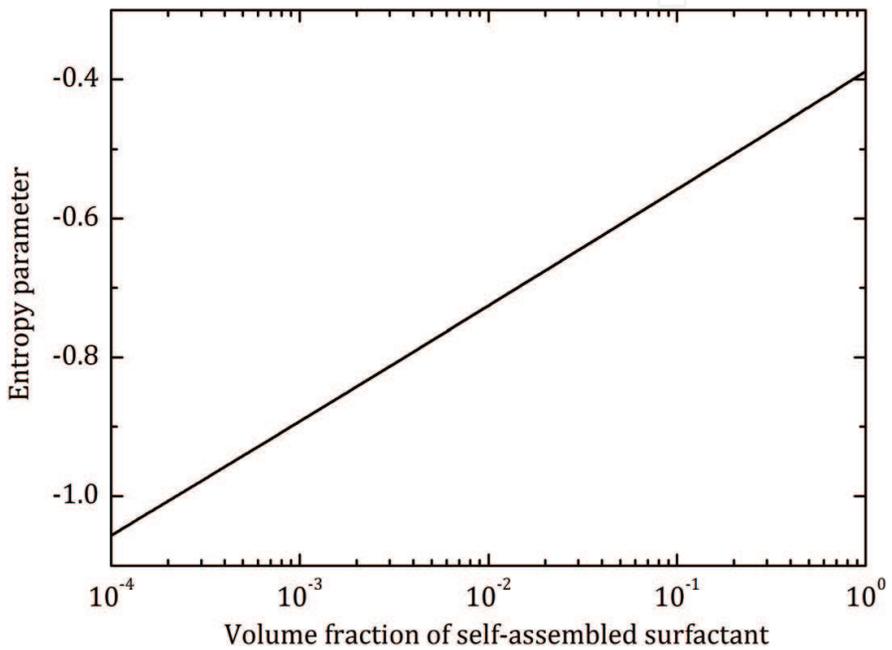

Figure 3. The self-assembly entropy parameter k_s plotted against the volume fraction ϕ_s of self-assembled surfactant, in accordance with Eq. (20). The three bending elasticity constants k_c, $\overline{k}_c$ and H_0 assume identical values as in **Figure 2**.

5. Average droplet size

The following expression for the (volume weighted) average droplet radius may be derived from the size distribution in Eq. (16)

$$\langle R \rangle = \frac{1}{\phi_d} \int_0^\infty R \phi_d dR = \frac{k_{eff}}{2k_c H_0} \frac{1}{x} \tag{23}$$

where the quantity

$$x = \frac{\sqrt{\pi\alpha}(2\alpha + 1)(1 + erf\sqrt{\alpha}) + 2\alpha e^{-\alpha}}{\sqrt{\pi\alpha}(2\alpha + 3)(1 + erf\sqrt{\alpha}) + 2\alpha e^{-\alpha} + 2e^{-\alpha}} \tag{24}$$

only depends on α. For sufficiently large values of α, Eq. (24) may be simplified so as to give

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$$\frac{1}{x} = \frac{2\alpha + 3}{2\alpha + 1} = 1 + \frac{2}{2\alpha + 1} = 1 + \frac{2}{8\pi k_{eff}/kT + 1} \tag{25}$$

Combining Eqs. (23) and (25) gives the following rather simple expression for the average droplet radius

$$\langle R \rangle = \frac{k_{eff}}{2k_c H_0}\left(1 + \frac{2}{8\pi k_{eff}/kT + 1}\right) \tag{26}$$

According to Eqs. (23) and (26), the average droplet size depends on k_{eff} as well as on $k_c H_0$ and in **Figure 4** we have plotted $\langle R \rangle$ against k_{eff} for a certain value of $k_c H_0$ corresponding to a gemini surfactant that forms elongated micelles in water [13]. It is seen that the more simple equation (26) is an excellent approximation in virtually the entire regime of k_{eff} values. As expected, $\langle R \rangle$ is found to increase considerably with increasing values of $\overline{k}_c$ as well as decreasing values of H_0. The dependence on the more shape-related bending rigidity is more complex. For the case where $k_c \gg \overline{k}_c + k_s$, Eq. (26) simplifies to $\langle R \rangle = 1/H_0$ and droplet size only depends on spontaneous curvature. For small k_c values, however, the size of the droplets is explicitly determined by the quantity k_c times H_0.

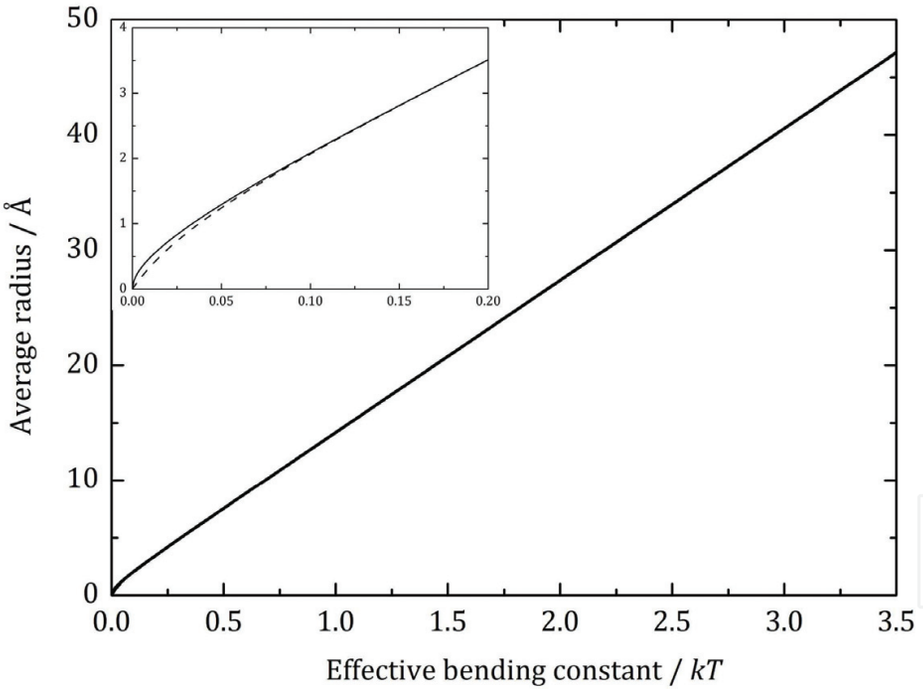

Figure 4. The average radius $\langle R \rangle$ of microemulsion droplets plotted against effective bending constant k_{eff} in accordance with Eqs. (23) and (24) (solid line) and Eq. (26) (dashed line). The spontaneous curvature H_0 was set to the same value as in **Figure 2**.

In addition to the three bending elasticity constants, the droplet size also depends on the self-assembly entropy parameter k_s. The always negative parameter k_s reduces the size of the droplets and its effect becomes stronger as the concentration of droplets decreases. As a result, microemulsion droplets grow in size with increasing surfactant concentration (cf. **Figure 2**). We may note that the expression $\langle R \rangle = (2k_c + \overline{k}_c)/2k_c H_0$, according to which $\langle R \rangle$ does not

depend on surfactant concentration, was derived by Safran [24] for the case where self-assembly entropy effects were neglected. This is the optimal value of $\langle R \rangle$, obtained for the case where only bending elasticity properties are considered. As a matter of fact, the Safran equation is recovered as a special case of Eq. (26) in the limit $2k_c + \overline{k}_c \rightarrow \infty$, as k_s becomes negligible. Since k_s is always negative, the size of the droplets must be smaller than the value predicted by the Safran equation (cf. **Figure 2**).

6. Polydispersity

Like average droplet size, microemulsion droplet polydispersity may be predicted from the present model. From the size distribution function in Eq. (16), we may derive the following expression for the average of the squared radius

$$\langle R^2 \rangle = \frac{1}{\phi_{drop}} \int_0^\infty R^2 \phi(R) dR = \left(\frac{k_{eff}}{2k_c H_0} \right)^2 \frac{1}{y} \tag{27}$$

where

$$y = \frac{\sqrt{\pi} 2\alpha(2\alpha+1)(1+erf\sqrt{\alpha}) + 4\alpha^{3/2} e^{-\alpha}}{\sqrt{\pi}(4\alpha^2+12\alpha+3)(1+erf\sqrt{\alpha}) + 2\alpha^{1/2}(2\alpha+5)e^{-\alpha}} \tag{28}$$

Hence, the polydispersity in terms of the relative standard deviation equals

$$\frac{\sigma_R}{\langle R \rangle} = \sqrt{\frac{\langle R^2 \rangle}{\langle R \rangle^2} - 1} = \sqrt{\frac{x^2}{y} - 1} \tag{29}$$

in accordance with Eqs. (23) and (27) and where the definition of x is given in Eq. (24). Equation (29) may be simplified so as to give the following excellent approximation for the polydispersity as a function of $\alpha = 4\pi k_{\text{eff}}/kT$ (cf. **Figure 5**).

$$\frac{\sigma_R}{\langle R \rangle} = \sqrt{\frac{4\alpha^2+3}{2\alpha(2\alpha+3)^2}} = \sqrt{\frac{1}{6\alpha} + \frac{2}{6\alpha+9} - \frac{4}{(2\alpha+3)^2}} \tag{30}$$

The polydispersity according to Eqs. (29) and (30), respectively, is plotted in **Figure 5**. Notably, the droplet polydispersity does not at all depend on spontaneous curvature, but is seen to be a sole function of $k_{eff} = 2k_c + \overline{k}_c + k_s$. This means that k_{eff} may be directly determined from experimentally available polydispersities. It is seen that $\sigma_R/\langle R \rangle$ decreases with increasing values of the effective bending constant and it approaches $\sigma_R/\langle R \rangle = \sqrt{kT/8\pi k_{eff}}$ in the limit of large k_{eff}. The latter expression (with $k_s = 0$) was first derived by Milner and Safran for the case where self-association entropy effects were neglected [7]. Since the entropy parameter k_s depends on surfactant concentration [cf. Eq. (22)], $\sigma_R/\langle R \rangle$ according to Eq. (30) is predicted to decrease with increasing surfactant concentration.

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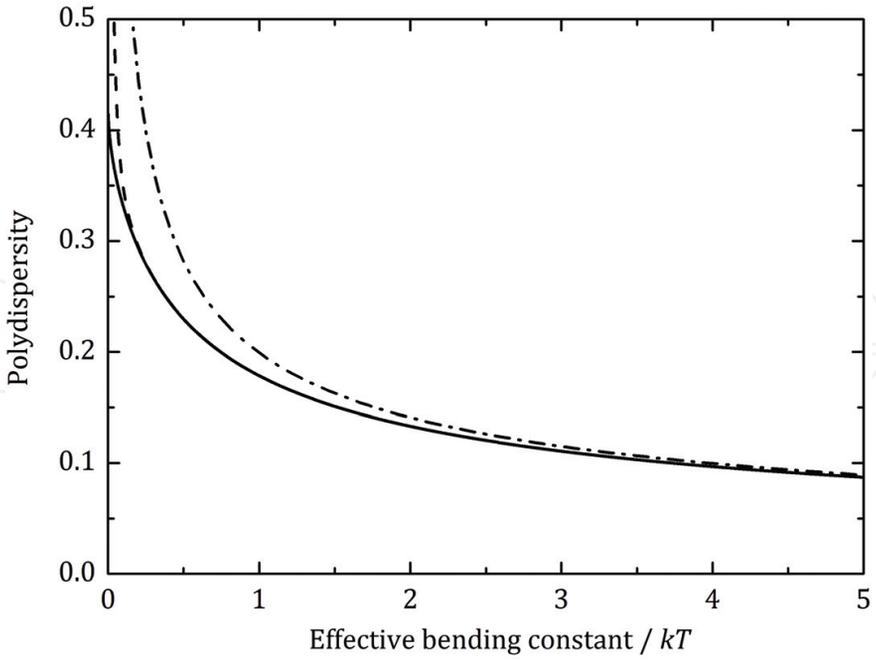

Figure 5. The relative standard deviation $\sigma_R/\langle R\rangle$ plotted against effective bending constant k_{eff} in accordance with Eq. (29) (solid line) and Eq. (30) (dashed line) as well as according to the approximate expression $\sigma_R/\langle R\rangle = \sqrt{kT/8\pi k_{\text{eff}}}$ (dash-dotted line).

7. Interfacial tension

The (planar) interfacial tension between the water and oil phases in a microemulsion in equilibrium with excess solvent phase is an experimentally available quantity. Hence, it has been observed that unusually small interfacial tensions are, in general, generated in microemulsion systems. The values are found to decrease in magnitude as the droplet size increases and may approach as low values as 10^{-3}–10^{-2} mNm^{-1} in non-ionic surfactant microemulsion systems at the phase inversion temperature (PIT) [10, 25].

From our present model we obtain the planar interfacial tension γ_p from the definition of k_{eff} in Eq. (19), i.e.

$$\gamma_p = \frac{4(k_c H_0)^2}{k_{eff}} \tag{31}$$

Similar to droplet size, the interfacial tension depends on the three bending elasticity constants as well as the entropy parameter k_s. In **Figure 6** we have plotted γ_p against the effective bending constant k_{eff} for some different values of the spontaneous curvature H_0. It is seen that γ_p decreases significantly as k_{eff} is increased or H_0 is reduced. For spontaneous curvatures approaching the limit $H_0 = 1/4\xi$, where bilayer structures start to form in aqueous solvents [26], γ_p may drop well below 1 mNm^{-1}. Notably, γ_p decreases with increasing surfactant concentration and droplet volume fraction since it, according to Eq. (31), depends on the entropy parameter k_s.

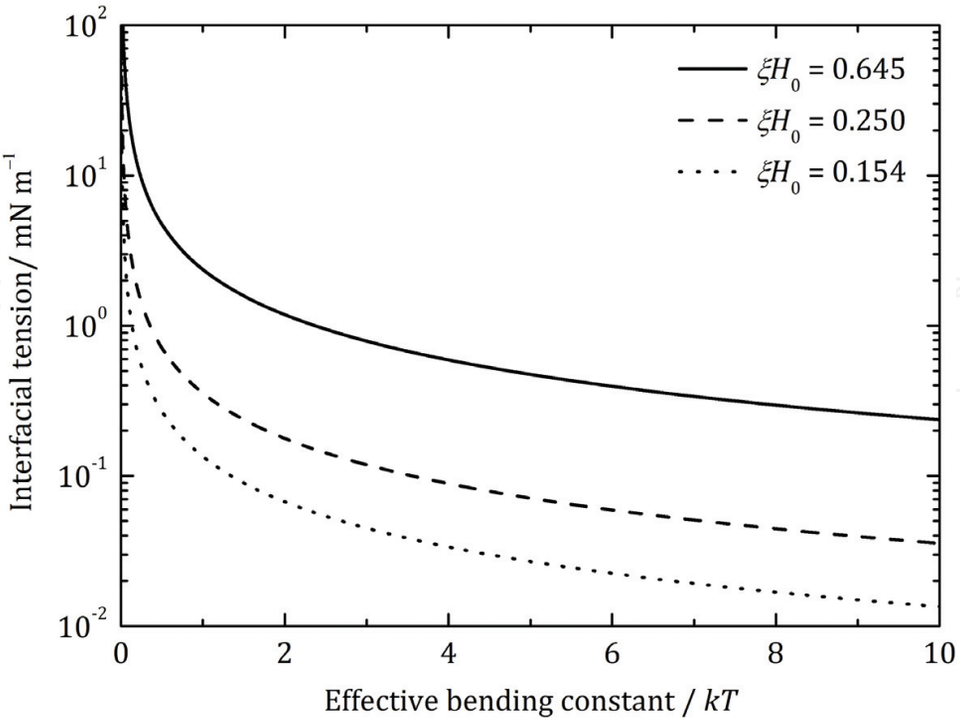

Figure 6. The planar interfacial tension γ_p of microemulsions plotted against effective bending constant k_{eff} in accordance with Eq. (31) for some different values of the spontaneous curvature H_0.

By means of combining Eqs. (26) and (31), we may eliminate $k_c H_0$ to deduce the following expression that relates interfacial tension and droplet size

$$\gamma_p = \frac{k_{eff}}{\langle R \rangle^2}\left(1 + \frac{2}{8\pi k_{eff}/kT + 1}\right)^2 \tag{32}$$

According to Eq. (32), the interfacial tension must decrease in magnitude as the size of the droplets increases (cf. **Figure 7**). This behaviour agrees very well with experimental observations that surfactants forming larger microemulsion droplets are, in general, found to have smaller interfacial tensions. γ_p is seen to drop below 1 mNm^{-1} as the radius exceeds a few nanometres for some typical value of $2k_c + \overline{k}_c$. Moreover, the interfacial tension is seen to fall below about 0.01 mNm^{-1} as the droplet size approaches orders of magnitudes equal to 1 μm. These values agree very well with observations of minimum interfacial tensions obtained for microemulsions formed by temperature sensitive non-ionic surfactants at PIT, where the microemulsion contains equal amounts of oil and water [10].

Since k_{eff} is directly related to the droplet polydispersity, it may, in principle, be eliminated by means of combining Eqs. (30) and (32) to yield a relation between the three experimentally available quantities $\langle R \rangle$, $\sigma_R/\langle R \rangle$ and γ_p. The following approximate expression (valid for polydispersities lower than about $\sigma_R/\langle R \rangle$ = 0.1) is obtained by means of inserting $\sigma_R/\langle R \rangle = \sqrt{kT/8\pi k_{eff}}$ in Eq. (32)

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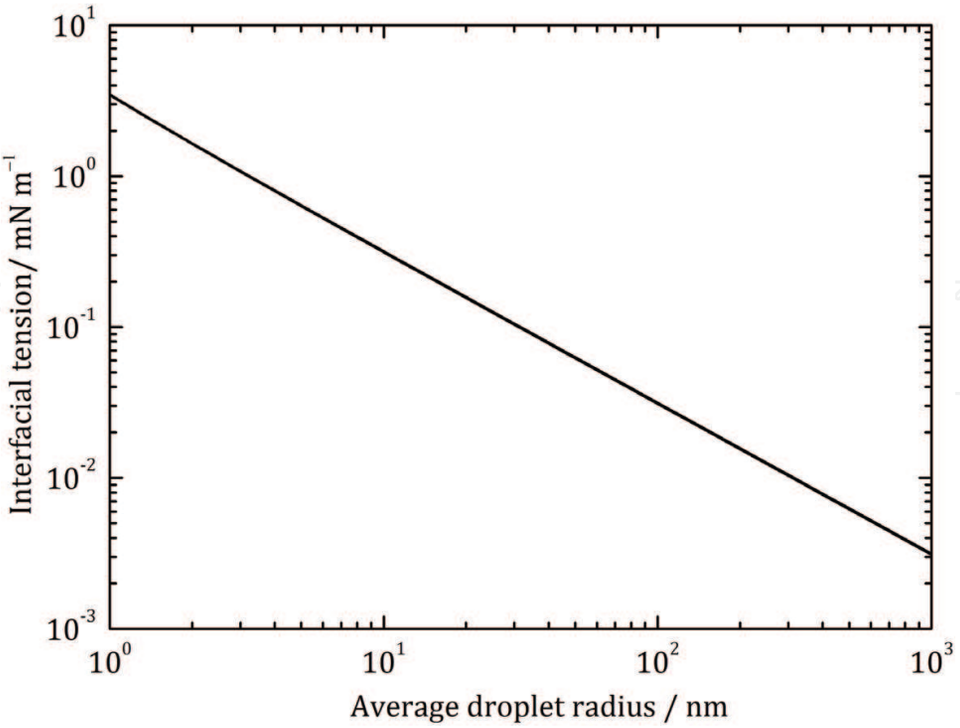

Figure 7. The planar interfacial tension γ_p of microemulsions plotted against the average droplet radius $\langle R \rangle$ in accordance with Eq. (32).

$$\gamma_p = \frac{kT}{8\pi \langle R \rangle^2 (\sigma_R / \langle R \rangle)^2} \left(1 + \frac{2}{(\sigma_R / \langle R \rangle)^{-2} + 1} \right)^2 \tag{33}$$

The relation between interfacial tension, droplet radius and polydispersity may also be expressed in terms of the dimensionless parameter [27]

$$w \equiv 8\pi \left(\frac{\sigma_R}{\langle R \rangle} \right)^2 \frac{\gamma_p \langle R \rangle^2}{kT} \tag{34}$$

Combining Eqs. (26), (30) and (31), the following approximate expression for w may be derived

$$w = \frac{4\alpha^2 + 3}{(2\alpha + 1)^2} = 1 - \frac{2(8\pi k_{eff} - 1)}{(8\pi k_{eff} + 1)^2} \tag{35}$$

In the limit $k_{\text{eff}} \rightarrow \infty$ (equivalent to $\sigma_R / \langle R \rangle \rightarrow 0$), Eq. (35) may be further simplified so as to give $w = 1$, the expression of which has been derived by Gradzielski et al. [27] for the case where self-association entropy effects were neglected. It is necessary that γ_p assumes low values for a system of small droplets, with a large overall interfacial area, to form. The ultra-low values of interfacial tensions experimentally observed in microemulsion systems appear as a consequence of the comparatively large interfacial area between oil and water that is formed in colloidal systems consisting of small droplets. Microemulsions are thermodynamically equilibrated systems and the

disadvantageous (positive) free energy of increasing the interfacial area is exactly balanced by the favourable (negative) free energy of mixing oil droplets with solvent water. The entropy of mixing increases with the number of dissolved droplets, equivalent to a reduction in droplet size, and the corresponding contribution to the free energy becomes increasingly more negative with decreasing droplet size. As a result, the interfacial tension must decrease in magnitude with increasing droplet size in accordance with Eq. (33).

8. Solubilisation

A notable property of microemulsion systems is the ability to dissolve hydrophobic components which otherwise are insoluble in an aqueous solvent. A quantitative measure of the solubilisation capacity may be considered as the ratio of the volume of oil (V_{oil}) that is solubilized and the volume of surfactant (V_{surf}) present in the solution. Hence, we may define the solubilisation capacity as follows

$$\sigma \equiv \frac{V_{\text{oil}}}{V_{\text{surf}}} \tag{36}$$

Since the surfactant is exclusively located at the droplet interface whereas the oil molecules are confined to the interior of the droplets, σ becomes strongly dependent on droplet size. The volumes of solubilized oil and aggregated surfactant, respectively, are obtained from the following geometrical relations valid for spherical droplets with an average radius $\langle R\rangle$ and an interfacial surfactant monolayer with thickness ξ (*cf*. **Figure 1**)

$$V_{\text{oil}} = N_{\text{drop}} \cdot \frac{4}{3}\pi(\langle R\rangle - \xi)^3 \tag{37}$$

$$V_{\text{surf}} = N_{\text{drop}} \cdot \frac{4}{3}\pi\langle R\rangle^3 - V_{\text{oil}} = N_{\text{drop}} \cdot \frac{4}{3}\pi[\langle R\rangle^3 - (\langle R\rangle - \xi)^3] \tag{38}$$

where N_{drop} is the total number of droplets. Combining Eqs. (36)–(38) gives the following expression for the solubilisation capacity

$$\sigma = \frac{1 - \delta^3 + 3\delta^2 - 3\delta}{\delta^3 - 3\delta^2 + 3\delta} \tag{39}$$

as a function of the single quantity δ defined as

$$\delta \equiv \frac{\xi}{\langle R\rangle} = \frac{2k_c\xi H_0}{k_{\text{eff}}}\left(1 - \frac{2}{8\pi k_{\text{eff}}/kT + 3}\right) \tag{40}$$

The second equality in Eq. (40) is obtained by means of employing the expression in Eq. (26) for the average droplet radius.

In **Figure 8**, we have plotted the average droplet radius $\langle R\rangle$ against the volume fraction of surfactant self-assembled in the droplet interfaces. It is seen that the droplet size increases with an increasing surfactant concentration as a result of the self-association entropy effects

discussed above. This means that we obtain an enhanced solubilisation effect as the amount of added surfactant is increased. The number of droplets, as well as the average size of the droplets, increases as the surfactant concentration is raised and both effects contributes to an increased solubilisation capacity.

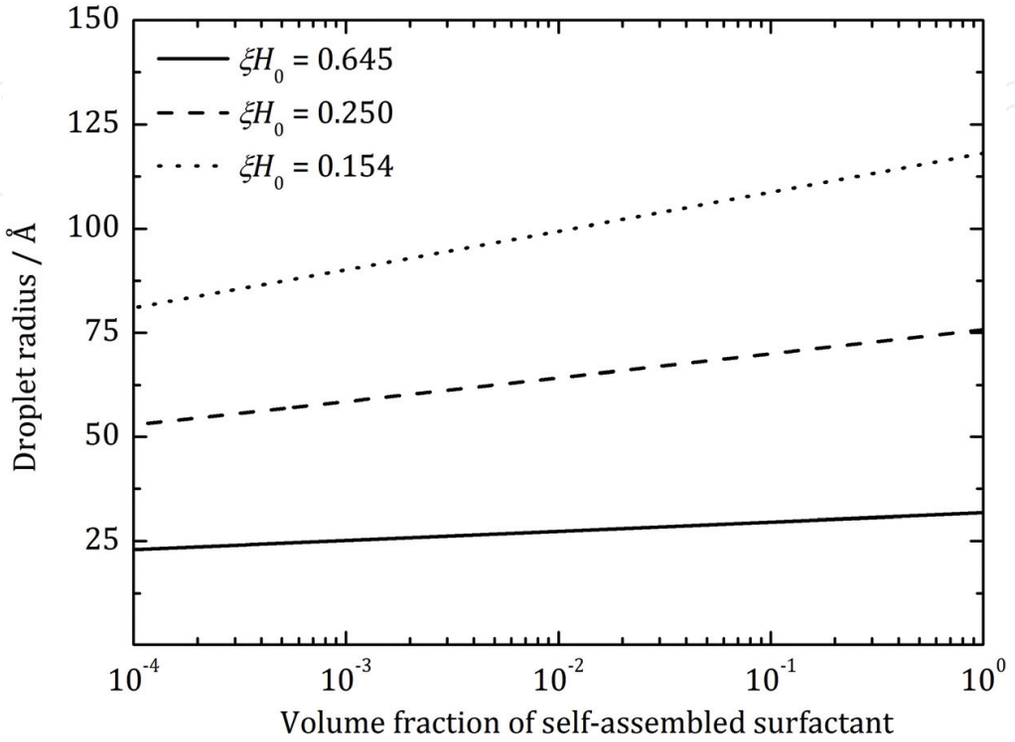

Figure 8. The average radius $\langle R \rangle$ of microemulsion droplets plotted against the volume fraction φ_s of self-assembled surfactant in accordance with Eqs. (23) and (24) for some different values of the spontaneous curvature H_0. The bending rigidity k_c and saddle-splay constant $\bar{k}_c$ assume identical values as in **Figure 2**.

The solubilisation capacity σ, as defined in Eq. (39), is plotted against the surfactant concentration in **Figure 9**. It is seen that σ increases considerably with increasing surfactant concentration. σ strongly depends on the different bending elasticity constants. The bending rigidity k_c and saddle-splay constant $\bar{k}_c$ have been found to be of the order of magnitude kT for many common surfactants and the possibility to tune the values of them is usually limited [11]. The spontaneous curvature H_0, on the other hand, strongly depends on the surfactant HLB value and may assume values from close to zero, for amphiphilic molecules forming bilayers, to much higher values for surfactants forming small micelles. In **Figure 9** we have chosen to compare σ for three different values of H_0. The smallest value $\xi H_0 = 1.55^{-1} = 0.154 > 0.25$ corresponds to a (gemini) surfactant that form elongated micelles in an aqueous solution and the solubilisation capacity is found to be rather small, with σ considerably lower than unity. However, σ is found to increase substantially as the spontaneous curvature is decreased to $\xi H_0 = 0.25$, which corresponds to the point of transition from micelles to bilayers in an aqueous solvent in the absence of oil [26]. Further decreasing H_0 to $\xi H_0 = 6.5^{-1} = 0.645$, i.e. to values where rather large bilayer structures are expected to form, the solubilisation capacity σ exceeds unity, which means that the amount of oil that is dissolved exceeds the amount of surfactant present in the solution. As a matter of fact, these results agree very well with observations that the solubilisation

capacity of decane (oil) in mixed tetradecyldimethylamine oxide (TDMAO)-hexanol microemulsion droplets was found to be significantly larger at high hexanol compositions, where vesicles are formed in the absence of oil, as compared to compositions where mixed micelles form in the absence of oil [5].

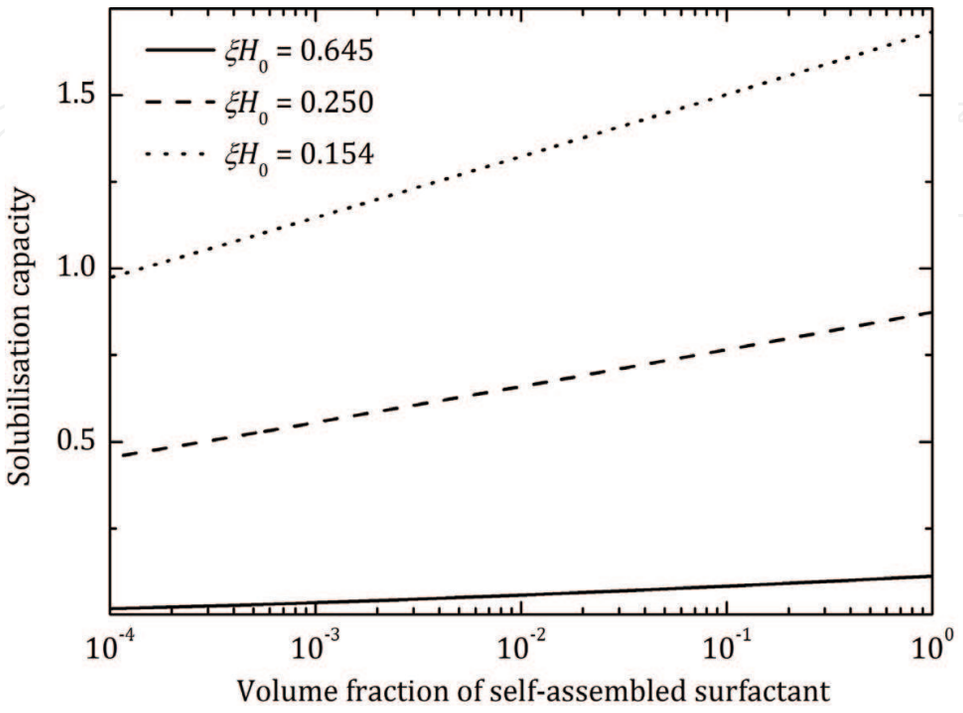

Figure 9. The solubilisation capacity σ of a microemulsion plotted against the volume fraction ϕ_s of self-assembled surfactant in accordance with Eq. (39) for some different values of the spontaneous curvature H_0. The bending rigidity k_c and saddle-splay constant $\bar{k}_c$ assume identical values as in **figure 2**.

9. Summary

A comprehensive theoretical model for the formation of microemulsion droplets has been presented. The theory is based on thermodynamics of self-assembling surfactant molecules aggregated in the droplet interfaces, combined with bending elasticity properties of the surfactant monolayer as taken into account by the three parameters spontaneous curvature, bending rigidity and saddle-splay constant. It relates properties depending on surfactant chemical structure with experimentally available properties of the droplets, such as average size, polydispersity, interfacial tension and solubilisation capacity. It has recently been demonstrated that all three constants H_0, k_c and $\bar{k}_c$ may be determined from measurements of growth behaviour of surfactant micelles in aqueous solutions (in the absence of oil). [12, 13, 22] Hence, from the present model it is possible to predict, for instance, the solubilisation capacity of oil of a certain surfactant by studying the growth behaviour of micelles that is formed by the surfactant in the absence of oil.

Likewise, it is possible to determine the various bending elasticity constants by means of measuring the average droplet radius, polydispersity and/or interfacial tension of a microemulsion system. We have included the important contribution of entropy of self-assembly and, as a result,

we obtain quantitative expressions that differ from previously derived ones [7, 24, 27] where self-association entropy effects were omitted. Nevertheless, the previously derived expressions for average droplet radius, polydispersity and interfacial tension are all recovered as special cases from our model in the limit $2k_c + \bar{k}_c \to \infty$. Taking into account self-association entropy effects, quantified in terms of the parameter k_s, have the impact on the model to predict smaller values of the droplet size as compared to the case where the entropy of self-assembly is neglected. Moreover, k_s explicitly depends on surfactant concentration (k_s increases with increasing concentration), implying that the droplet size is predicted to increase, whereas the polydispersity decreases, with increasing surfactant concentration. Moreover, the model predicts ultra-low values of the interfacial tension that agrees excellently with experimental measurements [10, 25]. Likewise, the capacity to solubilize a hydrophobic component (oil) is predicted to increase dramatically by means of reducing the spontaneous curvature (equivalent to decreasing the HLB value) of the surfactant, in agreement with experiments. In addition, self-association entropy effects are shown to generate an enhanced solubilisation capacity as the size of the microemulsion droplets is found to increase with increasing surfactant concentration.

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